Electronic Supplementary Material (ESI) for Analyst.

Supporting Information

Flowing Gas in Mass Spectrometer:

Method for Characterization and Impact on Ion Processing

Xiaoyu Zhou, Zheng Ouyang*

Weldon School of Biomedical Engineering, Purdue University, West Lafayette, IN 47907

1. Electric Field Solving and Ion Trajectory Simulation

The electric potential, ψ, in free space is described by the Laplace equation,[1] which gives

$$\Delta\psi = 0 \quad \text{(S1)}$$

where $\Delta = \nabla^2$ is the Laplace operator. In this work, the electric field is solved via the "Electrostatics Module" of COMSOL program. The equation for the ion motion in electric field is as follow:[2-4]

$$m\frac{d^2u}{dt^2} = e\left[E_{DC} + E_{rf}\cos(\Omega t)\right] \quad (u = x, y \text{ or } z) \quad \text{(S2)}$$

where m is the mass, e is the charge, t is time, u is the displacement of the ion in the x, y or z direction. E_{DC} and E_{rf} represent the electric field strength of DC component and rf component at frequency Ω, respectively. An electric field can be expressed as the summation of the multipole fields, including the quadrupole, hexapole, octopole and higher-order fields.[2-4] In some specific cases, e.g., the electric field only contains linear quadrupole field as in ideal Paul trap, Equation 2 can be converted to the Mathieu equation and, thus, can be solved analytically. In most general cases, Equation 2 can be and needs to be solved numerically. In this work, the ion trajectory simulation in pure electric field was performed using the forth-order Runge-Kutta method.[3-5]

2. Gas Hydrodynamic Simulation and DSMC

At pressures lower than 1 torr, the mean free path of gas molecules is large and cannot be accurately described using the Navier-Stokes (NS) equations for continuum flow, which can be solved by standard computational fluid dynamics (CFD) techniques.[6-8] However, such gas flows can still be described using the Boltzmann equation,[9, 10] which can be solved by the Direct Simulation Monte-Carlo (DSMC) method.[9] The DSMC performs a direct simulation of the flow

with the statistical nature of the collisions dictated by the Boltzmann equation.[9, 11, 12] The DSMC uses a statistically representative number of molecules with defined physical size, with the number of simulated molecules varying from an order of several hundred in studies at earlier times to currently several millions in contemporary work with significantly improved computation capability.[13, 14] Each gas molecule moves freely between the collisions predicted by the statistics. The movement of the bulk flow is well described in the simulation results and the gas expansion in the atmospheric pressure interface of a mass spectrometer can be clearly characterized in the contour map of the gas speed.[15]

In this work, the gas hydrodynamic simulation was performed using DS2V program for DSMC (developed by Dr. Bird, Dept. of Aerospace Engineering, University of Sydney, Australia).[9] The flowchart of the DSMC simulation is shown in Fig. 1S.

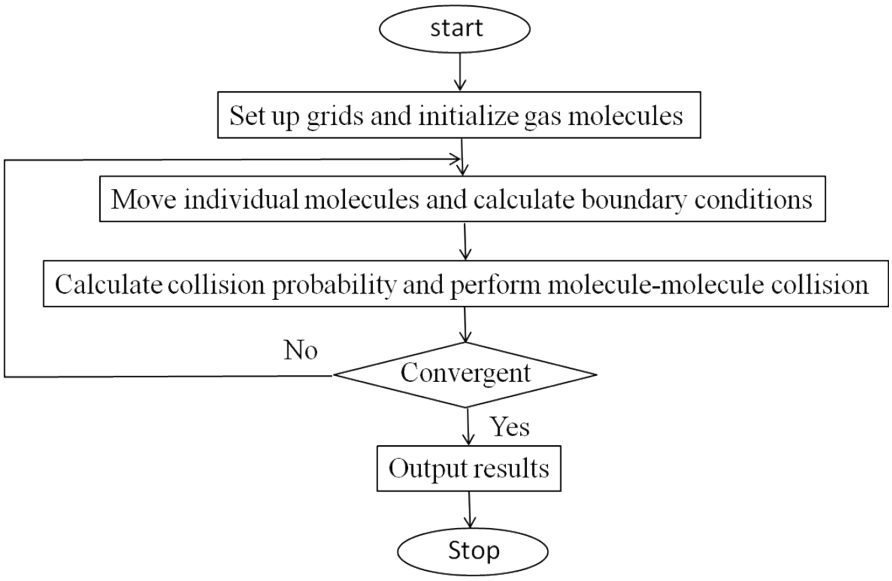

Figure 1S: Flowchart of DSMC method.

3. Hard-Sphere (HS) Collision Model

3.1 Formula of Ion-Gas Collision

HS is widely used to model particles in the statistical mechanical theory of gases.[9] Ions and gas molecules are assumed simply as impenetrable spheres that cannot overlap in space. During the collision, their momentum and energy must be conserved. This requires

$$m_{ion}\vec{v}_{ion} + m_{gas}\vec{v}_{gas} = m_{ion}\vec{v}'_{ion} + m_{gas}\vec{v}'_{gas} \quad \text{(S5)}$$

$$\frac{1}{2}m_{ion}v_{ion}^2 + \frac{1}{2}m_{gas}v_{gas}^2 = \frac{1}{2}m_{ion}v'^2_{ion} + \frac{1}{2}m_{gas}v'^2_{gas} \quad \text{(S6)}$$

where m_{ion} and m_{gas} are the masses of the ion and the gas molecule, $\vec{v}_{ion}$ and $\vec{v}_{gas}$ are the pre-collision velocity vectors of the ion and the gas molecule, $\vec{v}'_{ion}$ and $\vec{v}'_{gas}$ are the post-collision velocity vectors of the ion and the gas molecule, respectively. Because the direction of ion-gas collision is isotropic in HS model, the post-collision velocity of the ion is also isotropic, which gives

$$\vec{v}'_{ion} = \vec{v}_{ion} + \frac{2m_{gas}}{m_{ion} + m_{gas}}[(\vec{v}_{gas} - \vec{v}_{ion}) \cdot \vec{n}]\vec{n} \quad \text{(S7)}$$

where $\vec{n} = (\sin\theta\cos\varphi, \sin\theta\sin\varphi, \cos\theta)$ is an unit vector isotropic in spherical coordinate system, θ is inclination and φ is azimuth. The vector $\vec{n}$ can be generated by two random numbers, α_1 and α_2 , which distribute uniformly from 0 to 1 as following

$$\cos\theta = 1 - 2\alpha_1 \quad \text{(S8)}$$

$$\varphi = 2\pi\alpha_2 \quad \text{(S9)}$$

3.2 Sample of Gas Molecules

The ion is assumed to collide randomly with the gas molecules, whose velocity obeys the Maxwell distribution[9]

$$f(v_i) = \sqrt{\frac{m}{2\pi k_b T}} \exp[\frac{-m(v_i - v_{i0})^2}{2k_b T}], i = x, y, or\ z \quad \text{(S10)}$$

where v_i is the velocity of an individual gas molecule and v_{i0} is the velocity of the gas hydrodynamic field in the *i* direction, respectively. *T* is temperature of the hydrodynamic field. *m* is the mass of gas molecule. k_b is the Boltzmann constant. In EHS, the velocities of the gas molecules with a Maxwell distribution are generated by using the following equation with two random numbers, α_1 and α_2.

$$v_i = \sqrt{-\frac{2k_b T}{m} \ln(\alpha_1)} \cos(2\pi\alpha_2) \quad \text{(S11)}$$

3.3 Collision Probability

The probability of ion-gas collision is exponentially dependent upon the distance traveled in a time step and the average distance between collisions equals to the mean free path, λ_{ion}.[16, 17] In other words, the probability $P(L)$ of an ion that has a collision-free distance L between two collision events is

$$P(L) = e^{-L/\lambda_{ion}} \quad \text{(S12)}$$

The EHS method in this study used a random number α_1, of which the distribution was uniform from 0 to 1, to generate the free distance L with probability defined in Eq. (5)

$$L = -\lambda_{ion} \ln(\alpha_1) \quad \text{(S13)}$$

Herein, based on kinetic theory, the mean free path of the ion, λ_{ion} could be calculated by

$$\lambda_{ion} = \frac{k_b T}{\sigma p} \quad \text{(S14)}$$

where *p* and *T* are gas pressure and temperature, respectively. σ is the effective ion-gas collision cross-section, which in HS model is defined as

$$\sigma=\pi d_{eff}^2 \quad \text{(S15)}$$

where $d_{eff}=(d_{ion}+d_{gas})/2$ is the effective ion-gas collision diameter, d_{gas} is the diameter of the gas molecule, and d_{ion} is the diameter of the ion which can be evaluated from its m_{ion} by the following equation[18]

$$d_{ion}[\text{nm}]=0.120415405(m_{ion}[\text{amu}])^{1/3} \quad \text{(S16)}$$

4. Gas Dynamic Field and Ion Collision parameters

DSMC method can solve the flow field of neutral gas molecules that provides the properties of the flow such as velocity, pressure, temperature, mean free path, and Mach number, etc. The collision parameters of the ions can be derived from that of gas molecules. Use mean free path as an example, the mean free path of the ions λ_{ion}, according to Eq. (S14), is

$$\lambda_{ion}=\lambda_{gas}\sigma_{ion\text{-}gas}/\sigma_{gas\text{-}gas}. \quad \text{(S17)}$$

where λ_{ion} and λ_{gas} are the mean free paths of the ion and gas molecule, respectively. The cross sections of the ion $\sigma_{ion\text{-}gas}$ and gas molecules $\sigma_{gas\text{-}gas}$ can be calculated from Eqs. (S15) and (S16). From Fig. 2S, it can be found that the typical mean free path of the ion with m_{ion}=200 Da in the Einzel lens system is about λ_{ion}=1 mm.

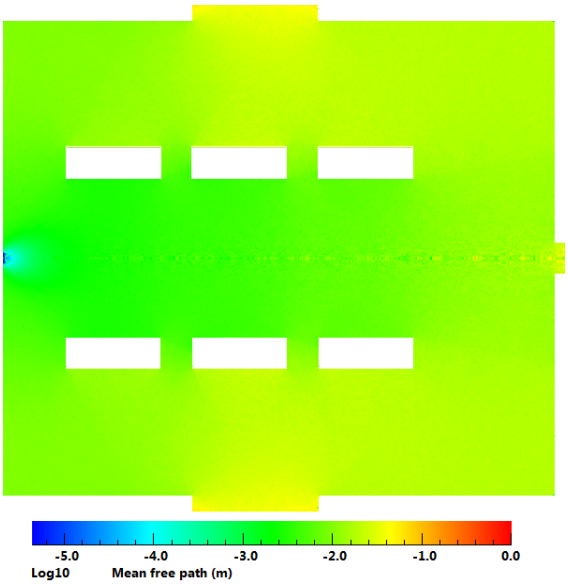

Figure 2S: The contour map of mean free path of gas molecules, λ_{gas}, in gas flow

Due to the large pressure difference, the flow speed in the downstream of the gas inlet is supersonic (i.e., Ma>1, Fig. 3S). In supersonic flow, the thermal energy of gas molecules is largely converted to bulk kinetic energy, where Ma is Mach number representing the ratio of flow speed to the local sound speed, $\sqrt{1.4k_bT/m_{gas}}$. Note that the sound speed can be used to evaluate the thermal movement of gas molecules because the mean thermal speed of gas molecules is $\sqrt{8k_bT/\pi m_{gas}}$. Hence, the mean time of between two ion-gas collisions can be evaluated by λ_{ion}/v_{ion}, where v_{ion} is the bulk speed of the flow field (Fig. 2b).

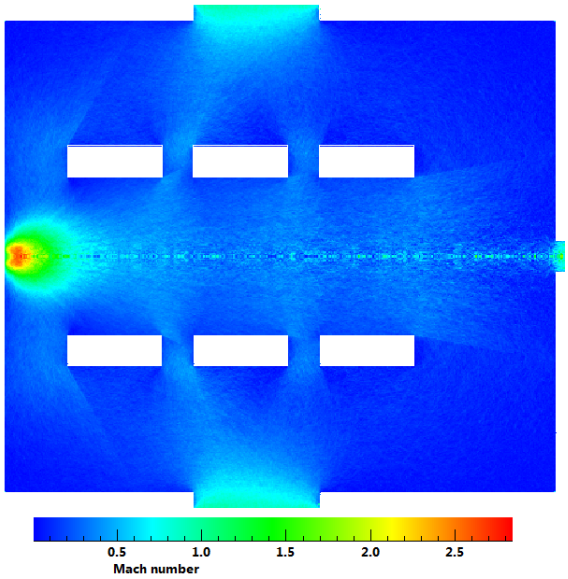

Figure 3S: The contour map of Mach number, Ma, of the gas flow.

Figure 4S

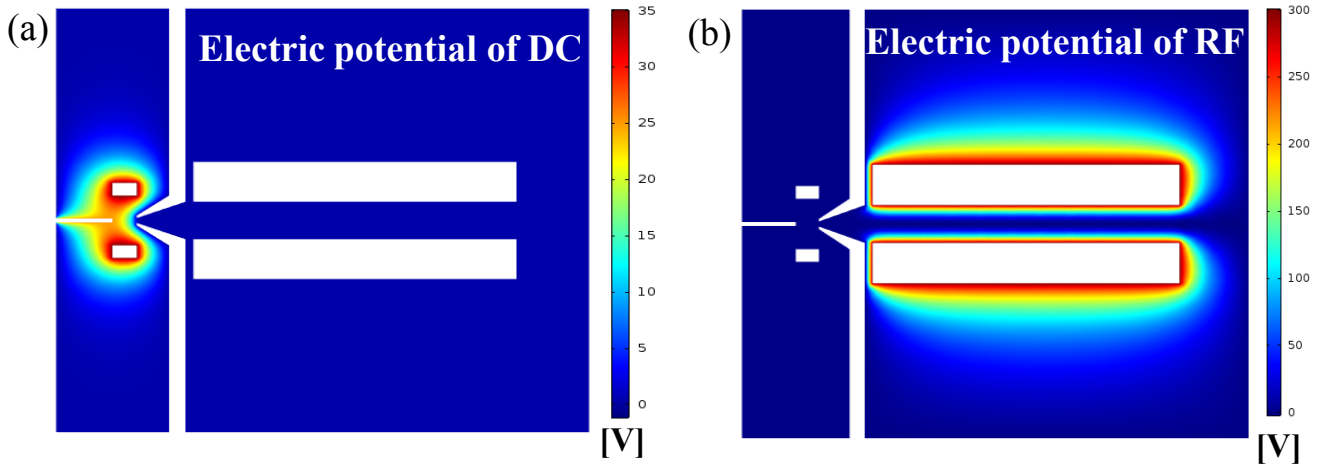

Figure 4S: The contour maps of electric potential of heated capillary-tube lens-skimmer assembly for: (a) DC and (b) RF.

Figure 5S

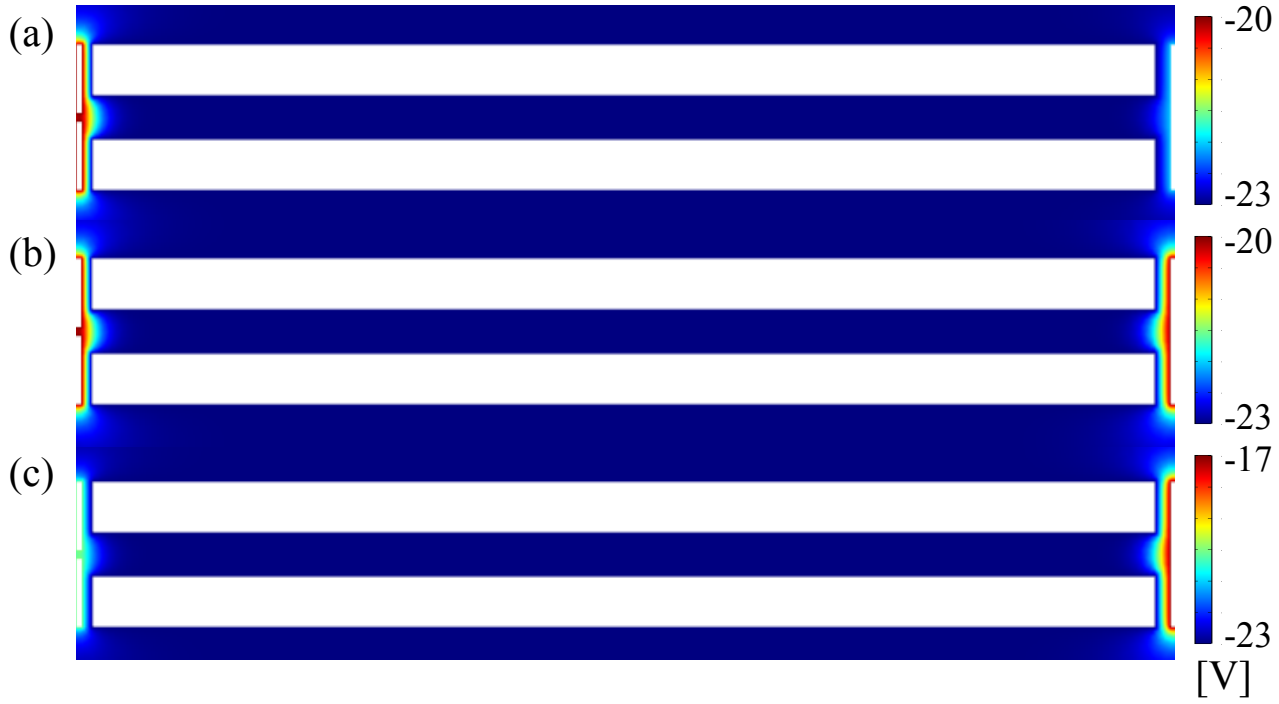

Figure 5S: The contour maps of DC electric potential of a linear ion trap in differential pumping stage for different exit lens potential: (a) -22 V, (b) -20 V and (c) -17 V. The DC voltages of Q3 entrance lens and Q3 are -20 and -23 V, respectively.

Figure 6S

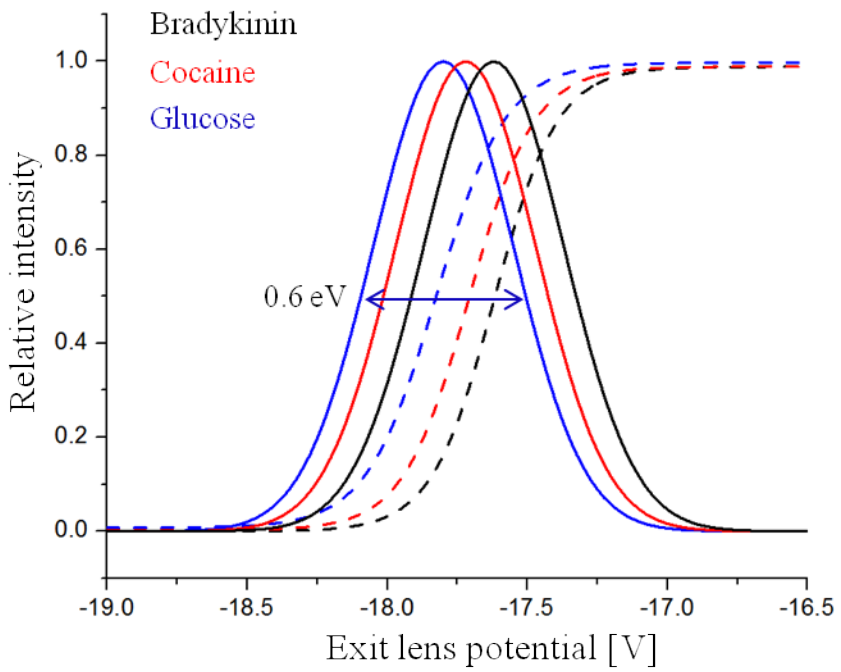

Figure 6S: Simulated energy distribution (solid curves) and relative signal intensity (dashed curves) as a function of the exit lens potential for: $[Glucose + H]^+$ (blue), $[Cocaine + H]^+$ (red), $[Bradykinin + 3H]^{3+}$ (black). The energy distribution is the derivation of the corresponding signal intensity.

References

1. W. H. Hayt and J. A. Buck, *Engineering electromagnetics*, 6th edn., McGraw-Hill, New York, **2001**.
2. E. D. Hoffmann and V. Stroobant, *Mass spectrometry: principles and applications*, 3rd edn., John Wiley & Sons Chichester, **2007**.
3. X. Zhou, G. Xu, C. Xiong, R. Chen, H. Qiao and Z. Nie, *Journal of Mass Spectrometry*, 2012, **47**, 286-293.
4. X. Zhou, C. Xiong, S. Zhang, N. Zhang and Z. Nie, *Journal of the American Society for Mass Spectrometry*, 2013, **24**, 794-800.
5. W. H. Press, S. A. Teukolsky, W. T. Vetterling and B. P. Flannery, *Numerical Recipes in Fortran 77, The Art of Scientific Computing. Vol. 1 of Fortran Numerical Recipes*, 2nd edn., Press Syndicate of the University of Cambridge, New York, **1992**.
6. F. M. White, *Fluid mechanics*, 7th edn., McGraw Hill, New York, **2011**.
7. C. B. Laney, *Computational gasdynamics*, Cambridge University Press, New York, **1998**.
8. F. Han, Y. Du, S. Cheng, Q. Zhou, C. Chen, KeyongHou, W. Wang and H. Li, *International Journal of Mass Spectrometry*, 2012, **309**, 13-21.
9. G. A. Bird, *Molecular gas dynamics and the direct simulation of gas flows*, Oxford University Press, New York, **1994**.
10. L. Viehland and W. Siems, *Journal of the American Society for Mass Spectrometry*, 2012, **23**, 1841-1854.
11. R. L. Spencer, J. Krogel, J. Palmer, A. Payne, A. Sampson, W. Somers and C. N. Woods, *Spectrochimica Acta Part B: Atomic Spectroscopy*, 2009, **64**, 215-221.
12. N. Gimelshein, S. Gimelshein, T. Lilly and E. Moskovets, *Journal of the American Society for Mass Spectrometry*, 2014, **25**, 820-831.
13. E. S. Oran, C. K. Oh and B. Z. Cybyk, *Annual Review of Fluid Mechanics*, 1998, **30**, 403-441.
14. E. P. Muntz, *Annual Review of Fluid Mechanics*, 1989, **21**, 387-417.
15. S. Garimella, X. Zhou and Z. Ouyang, *Journal of the American Society for Mass Spectrometry*, 2013, **24**, 1890-1899.
16. S. T. Quarmby and R. A. Yost, *International Journal of Mass Spectrometry*, 1999, **190/191**, 81-102.
17. D. J. Douglas and J. B. French, *Journal of the American Society for Mass Spectrometry*, 1992, **3**, 398-408.
18. A. D. Appelhans and D. A. Dahl, *International Journal of Mass Spectrometry*, 2005, **244**, 1-14.